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(19)

(54) IMPROVEMENTS IN OR RELATING TO MOULDING COMPOSITIONS

(71) We, DR. BECK & CO. AKTIENGESELLSCHAFT, of Hamburg 28, Eiselensweg, Germany, a German company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to moulding compositions for the manufacture of self-extinguishing synthetic resin mouldings.

It is well-known to manufacture self-extinguishing mouldings from moulding compositions based on unsaturated polyesters. Such moulding compositions contain polyesters incorporating greater or lesser amounts of halogens such as chlorine and bromine and possibly also synergistic materials, such as compounds of phosphorus and antimony, additionally incorporated into the resin molecule or added as fillers or softeners. Suitable formulations of such moulding compositions enable mouldings to be produced which, even after repeated exposure to the action of a flame or intensive ignition source, extinguish themselves on removal from the source within seconds; during ignition and thereafter, a loss of organic material occurs which, in the case of mouldings have good self-extinguishing properties and after repeated exposure to a flame can lead to the complete loss of the organic (and hence combustible) material without any independent continued burning over a protracted period of time being observed at all.

Although mouldings of this kind do not assist in the spreading of a fire, they do not represent a viable technical solution. The action of flame or other ignition source gives rise to the formation of corrosive gases, such as hydrogen chloride and hydrogen bromide, which can themselves produce severe damage to buildings and equipment, even where there has been no direct exposure to a flame.

It is well known that the self-extinguishing properties of mouldings can be improved by using moulding compositions containing aluminium hydroxide as a filler. For example, anti-tracking insulating material for use in electrical equipment, is described in British Patent Specification No. 831,490, comprising a polyester resin filled with aluminium hydroxide.

German Patent Specification No. 1182427, as laid open to public inspection, describes a moulding composition with a basis of a chlorine-containing saturated polyester and containing aluminium hydroxide as a filler. The insulators manufactured from such a composition exhibit improved tracking resistance and improved flame resistance.

In Modern Plastics 1965, page 202, a polyester premix system filled with aluminium hydroxide is stated to be comparable, at a 30% resin content, with a system comprising a halogen-bearing resin and antimony oxide so far as flame resistance is concerned. Again, the use of nitrogen compounds, such as melamine or cyanuric acid, has already been proposed. According to German Patent Specification No. L 15 202, in the case of cast resin insulators subjected to electric arcing, the tracking resistance is improved by the addition of nitrogen-containing compounds, such as melamine.

British Patent Specification No. 1,130,121 also describes unsaturated polyester resin compositions containing melamine or cyanuric acid as filler, for application in the cast resin field; these compositions give mouldings with improved tracking resistance.

The stress due to the arc is relatively small, so that even small additions of aluminium hydroxide, or melamine, or cyanuric acid, will suffice to produce adequate tracking resistance.

To obtain good self-extinguishing properties, however, very large additions of these fillers are needed. By the term "self-extinguishing properties" it is intended to indicate the above-described behaviour in which, under the action of a flame, the organic constituents of the moulding are completely destroyed although at no point is any inde-

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pendent continued burning for a protracted period of time observed. To obtain such properties, three parts by weight of the fillers in question must be used to one part by weight of combustible organic material. It has already been mentioned that correspondingly smaller additions produce an adequate effect if a halogen-containing organic compound is also included. Mouldings of this kind, however, lead in the event of fire to the secondary damage previously referred to.

For the manufacture of mouldings, a variety of technical processes are available. For many purposes, thermosetting mouldings are of particular interest. In order to manufacture such mouldings, a moulding composition is hardened during forming. The forming operation can in this connection, be carried out under normal pressure by simple casting, or under elevated pressure involving a moulding operation. For application as casting resins, only those moulding compositions can be used which have a sufficiently low viscosity to enable forming to take place without the application of external pressure.

By the addition of fillers to liquid moulding compositions, the viscosity is increased. With very high filling factors of the kind required to achieve adequate self-extinguishing properties by the use of fillers of the kind referred to above, the increase in viscosity is such that processing by casting is no longer possible. Although it is now known that such fillers impart flame-extinguishing properties, this capability has not been exploited in casting resin systems because the increase in viscosity encountered was thought to be excessive. It is accordingly an object of the present invention to provide moulding compositions for the production of self-extinguishing cast resins in which the advantageous properties of aluminium hydroxide and melamine or cyanuric acid are made use of in the cast resin field.

It has been found that when using unsaturated polyester resins modified by the presence of cyclic imide groups (the manufacture of which resins has already been described), then in order to achieve good self-extinguishing properties, a smaller amount of such fillers is needed than with ordinary polyester resins, so that moulding compositions are obtained which can be processed by casting.

This is surprising because both unsaturated polyester resins without any imide groups, and unsaturated polyester resins with imide groups, burn equally well.

According to the invention, there is provided a moulding composition comprising the following ingredients:—

(a) 30 to 40% by weight of the total of a polyester component consisting of or including a halogen-free unsaturated polyester containing cyclic imide groups with a cyclic imide group nitrogen content of at least 0.3% by weight of the polyester;

(b) 5 to 25%, by weight of the total of aluminium hydroxide; and

(c) 35 to 65% by weight of the total of melamine and/or ammeline and/or ammelide and/or cyanuric acid,

the percentages totalling 100%.

Besides at least one α,β-unsaturated dicarboxylic acid, at least one polyhydric alcohol, the starting materials for the polyester may also include at least one monohydric alcohol and/or at least one mono or poly-basic saturated, aliphatic, cycloaliphatic, or aromatic carboxylic acid; at least one of the starting materials providing cyclic imide groups in the final polyester.

The moulding composition may, if desired, include at least one copolymerisable monomer, together with a polymerisation initiator and, if desired, a polymerisation accelerator and/or a polymerisation inhibitor, the monomer, initiator and accelerator and/or inhibitor when present being counted in with the polyester for the purpose of calculating the proportions of polyester and fillers in the composition.

The preferred component range of the invention is shown by cross-hatching in the triangular graph shown in the accompanying drawing.

The moulding compositions of the present invention may accordingly contain (1) aluminium hydroxide, (2) melamine and/or ammeline and/or ammelide and/or cyanuric acid, (3) a condensation product of maleic acid and/or fumaric acid with one or more polyhydric alcohols, and possibly also one or more monohydric alcohols, together with, if desired, one or more other monobasic or polybasic carboxylic acids, at least one of the components used containing cyclic imide groups, (4) at least one monomeric copolymerisable substance, such as, for example, styrene, acrylic acid esters and substituted vinylbenzenes, (5) substances, such as organic peroxides, which initiate polymerisation, and (7) possibly substances such as tertiary aromatic amines or cobalt soaps, which accelerate polymerisation. As far as the application of the moulding compositions of the invention is concerned, it is advantageous to produce mixtures of all the components of the moulding composition with the exception of the compounds which initiate polymerisation; such mixtures have adequate storage properties and can be dispatched by normal means of transport. They can then, after the addition of the substances which initiate polymerisation, be hardened to form mouldings in a short time at room temperature, or at slightly higher temperatures.

As those skilled in the art will appreciate, the electrical volume resistance and the dielectric loss factor of mouldings are impaired by the content of aluminium hydroxide. It would therefore be desirable to employ as the

filler which imparts the non-flammable property, nitrogen compounds only, such as melamine and cyanuric acid, if this were possible. The mouldings produced in this way, however, have less favourable properties when subjected to the action of a flame. These mouldings, after removal of the igniting flame and after being extinguished, tend to reignite even if very large amounts of the nitrogen compounds are included. The above mentioned mixtures have been found to be surprisingly suitable. Preferably, aluminium hydroxide of the formula $Al(OH)_3$ with a mean grain size of about 35 μ, and melamine with a mean grain size of about 20 μ will be used.

The moulding compositions in accordance with the invention can be used with advantage in all those electrical engineering insulating situations where improved fireproofing is required. Particularly useful fields of application include the impregnation of high voltage transformers and voltage multipliers in television sets, and the insulation of busbars in high voltage systems. Compared with the known moulding compositions used for the manufacture of self-extinguishing mouldings, the compositions of the present invention have the advantage that they can be processed under normal pressure, have good storage characteristics, have excellent self-extinguishing properties and have good electrical properties.

The invention will now be further described with reference to specific examples of compositions according to the invention and of compositions not according to the invention for comparison purposes. In the examples, all percentages and ratios are by weight.

I. *Manufacture of an unsaturated polyester (1) (standard product)*

Propylene glycol	3.3 mol	251 g
maleic anhydride	2 mol	196 g
Tetrahydrophthalic anhydride	1 mol	152 g
Hydroquinone		0.1 g

The starting materials listed above were heated in a one-litre three necked flask equipped with a stirrer, a thermometer and a distillation head, for six hours to a temperature of 190°C, and maintained for a further two hours at this temperature, whereafter 50 ml of aqueous distillate were distilled off. Subsequently, a slowly increasing vacuum was applied and condensation carried out at 190° and 30 mm Hg until the acid number was 40. The unsaturated polyester so obtained was mixed with 0.01% by weight (0.06 g) of benzoquinone and dissolved in 300 g of styrene. 1% of a 10% solution of cobalt octoate in styrene, calculated on the final end product, was then added.

II. *Manufacture of an unsaturated polyester (2) containing imide groups*

N-β-hydroxyethyltetrahydrophthalic imide	2 mol	390 g
Maleic anhydride	3 mol	294 g
Neopentyglycol	1 mol	104 g
Glycerol	1 mol	104 g
Hydroquinone		0.1 g

In a manner similar to the manufacture of the polyester (1) an unsaturated polyester was produced from the starting materials listed above, which, after completion of the vacuum condensation phase, has an acid number of 25. After the addition of 0.1 g. of benzoquinone and 450 g of styrene together with 1% of a 10% cobalt octoate solution (calculated on the end product), an unsaturated polyester resin with a viscosity of 1000 cP was obtained.

As evidence of the surprising advantage of the resin modified by the imide groups over the standard resin, both materials were used with aluminium hydroxide F (a product produced by Martinwerke GmbH, Bergheim-Erft) to produce filled moulding compositions. In each case, after the addition of 1% of methylethylketone hydroperoxide, the moulding compositions were mixed in a 50% ratio with dimethyl phthalate, and poured into and hardened in test tubes of 15 mm internal diameter.

To assess the self-extinguishing properties, after removing the hardened mouldings from these test tubes, the mouldings were held at an angle of 45° above the tip of the blue cone of a Bunsen burner flame with a 6 cm cone length and 12 cm total flame length. The test rods were in each case subjected to the action of the flame for 15 seconds, after which the afterburning time was recorded. The test was repeated until an after-burning time of longer than 10 seconds was encountered. The number of ignitions up to this point is a measure of the quality of the self-extinguishing properties. It has been found that longer afterburning does not occur if more than 10 ignitions are used. From Table I below, it can be seen that the imide-modified, unsaturated polyester resin (2) filled in the ratio of 40 to 60% with aluminium hydroxide, satisfies the requirements imposed. The standard resin, however, even with a content of 70% aluminium hydroxide in the moulding, does not match up to the specifications. Moulding compositions with higher filler contents cannot be processed by the casting technique. Even with an aluminium hydroxide content below this level, the advantage of the imide modified resin is still clearly evident from Table I.

III. *Manufacture of an imide-modified, unsaturated polyester* (3)

N-β-hydroxyethyltetrahydrophthalic imide	1.9 mol	351 g
Maleic anhydride	1.2 mol	118 g
Neopentylglycol	5.4 mol	562 g
Trimethylolpropane	0.6 mol	80 g
Adipic acid	6.0 mol	876 g
Hydroquinone		0.01 g

N-β-hydroxyethyltetrahydrophthalic imide and maleic anhydride were introduced into the apparatus described with reference to the manufacture of the polyester (1) and heated to 80°C, whereupon an exothermic reaction commenced and the temperature rose to 130°C.

After this reaction, the remaining starting materials were added. Heating was then carried out to 210°C over 7 hours. After a further two hours at this temperature, the acid number was between 50 and 60. Thereafter, over a period of 2 hours, a vacuum was applied and raised to 30 mm Hg. At 210°C and 30 mm Hg, condensation was carried out for 2 hours after which the acid number had dropped to 21. The resultant polyester resin was dissolved in a ratio of 2:1 in styrene and mixed with 1% of a 10% cobalt octoate solution.

This resin, when hardened, yielded highly elastic mouldings. Moulding compositions, produced using this resin, are suitable as insulating coatings for quite large systems. With a resin of this kind, the disadvantageous electrical properties of the aluminium hydroxide, are particularly evident (see for example the dielectric constant in test 3 of Table II below). From the other tests in Table II the reason for the restriction of the content of aluminium hydroxide will be abundantly clear. If melamine only is used as the filler, then the self-extinguishing properties are inadequate (compare for example the ignitions in tests 4, 6 and 7 of Table II). Mixtures of aluminium hydroxide and melamine within the limits of the present invention (compare tests 1, 2 and 8 of Table II) are particularly suitable as far as number of ignitions and dielectric constants are concerned.

At least a part of the melamine may, if desired, be replaced by ammeline and/or ammelide, and/or cyanuric acid.

TABLE I

Test	1	2	3	4	5	6	7	8	9	10
Parts by weight of Polyester 2 containing imide groups		30		33		40		45		50
Parts by weight of Polyester 1 (Standard Product)	30		33		40		45		50	
Parts by weight $Al(OH)_3$	70	70	67	67	60	60	55	55	50	50
No. of ignitions	9	>10	6	>10	5	>10	4	9	1	6

TABLE II

Test	1	2	3	4	5	6	7	8
Parts by weight Polyester 3 containing imide groups	30	30	30	30	30	35	40	40
Parts by weight $Al(OH)_3$	5	25	70		40	0	0	5
Parts by weight Melamine	65	45		70	30	65	60	55
Methylethylketone peroxide 50%	1	1	1	1	1	1	1	1
No. of ignitions	>10	>10	>10	9	>10	6	3	10
Dielectric constant at 60°C.	5.2	5.2	7.0	5.1	5.5	5.1	5.1	5.1

WHAT WE CLAIM IS:—

1. A moulding composition comprising the following ingredients:—

(a) 30 to 40% by weight of the total of a polyester component consisting of or including a halogen-free unsaturated polyester containing cyclic imide groups with a cyclic imide group nitrogen content of at least 0.3% by weight of the polyester;

(b) 5 to 25% by weight of the total of aluminium hydroxide; and

(c) 35 to 65% by weight of the total of melamine and/or ammeline and/or ammelide and/or cyanuric acid,

the percentages totalling 100%.

2. A moulding composition as claimed in Claim 1, wherein the starting materials for the formation of said polyester include at least one α,β-unsaturated dicarboxylic acid or anhydride, at least one polyhydric alcohol, and optionally at least one monohydric alcohol and/or at least one mono or polybasic saturated aliphatic, cycloaliphatic or aromatic carboxylic acid, at least one of the starting materials serving to provide cyclic imide groups in the final polyester.

3. A moulding composition as claimed in Claim 1 or Claim 2, wherein said polyester component includes at least one monomer copolymerisable with said polyester and a polymerisation initiator.

4. A moulding composition as claimed in Claim 3, wherein said polyester component includes a polymerisation accelerator.

5. A moulding composition as claimed in Claim 3, or Claim 4, wherein said polyester component includes a polymerisation inhibitor.

6. A moulding composition as claimed in any one of Claims 3 to 5, wherein said copolymerisable monomer is styrene.

7. A moulding composition as claimed in any one of the preceding claims wherein said aluminium hydroxide has a mean grain size of about 35 μ.

8. A moulding composition as claimed in any one of the preceding claims wherein ingredient (c) is melamine having a mean grain size of about 20 μ.

9. A moulding composition as claimed in Claim 1, substantially as hereinbefore described with reference to Table II.

10. Self-extinguishing mouldings produced using a moulding composition as claimed in any one of the preceding claims.

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1 SHEET

COMPLETE SPECIFICATION

This drawing is a reproduction of the Original on a reduced scale.